Accessing the molecular frame through strong-field alignment of distributions of gas phase molecules

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Abstract: A rationale for creating highly aligned distributions of molecules is that it enables vector properties referenced to molecule-fixed axes (the *molecular frame*) to be determined. In the present work, the degree of alignment that is necessary in order for this to be achieved in practice is explored. Alignment is commonly parametrised in experiments by a single parameter**,** $\langle\cos^2\theta\rangle$, which is insufficient to enable predictive calculations to be performed. Here it is shown that, if the full distribution of molecular axes takes a Gaussian form, this single parameter can be used to determine the complete set of alignment moments needed to characterise the distribution. In order to demonstrate the degree of alignment that is required in order to approach the molecular frame, the set of alignment moments corresponding to a few chosen values of $\langle\cos^2\theta\rangle$ are used to project a model molecular frame photoelectron angular distribution into the laboratory frame. These calculations show that $\langle\cos^2\theta\rangle$ needs to approach 0.9 in order to avoid significant blurring to be caused by averaging.

Over the last decade or so there has been considerable interest in the use of strong electric fields, such as those produced by high intensity laser light, as a means of aligning and orienting the axes of gas phase molecules in space.[1-11] These techniques pave the way for the study of stereo-dynamical phenomena, including those associated with reaction dynamics[1, 12, 13] and photoionization,[14-18] as well as for the preparation of molecular targets for ultrafast diffraction experiments.[10, 19] However, in order to exploit the techniques quantitatively it is important to be able to characterize the prepared alignment or orientation in a set of basis functions that relate to the symmetry of the distribution of molecular axes.

A distribution of molecular axes, $P(\theta,\phi)$, that is aligned or oriented along one axis in space can be expressed as an expansion in spherical harmonics, $Y_{KQ}(\theta,\phi)$, where the polar angle θ and the azimuthal angle ϕ define the position of the principal molecular axis, lying along *z*, relative to a laboratory-fixed axis system (*X*,*Y*,*Z*):[20]

$$P(\theta,\phi) = \sum_{KQ} A_{KQ} Y_{KQ}(\theta,\phi) \ . \tag{1}$$

In Eq. (1) the A_{KQ} coefficients are moments of the molecular axis distribution defined by the rank (*K*) and component (*Q*), where $K = 0,1,2\ldots$, and $-K \le Q \le K$. The A_{00} term is proportional to the total number of molecules, and the higher A_{KQ} terms scale with A_{00}. For our purposes here, the distribution will be assumed to be normalized, so that

$$\int_0^{2\pi}\int_0^{\pi} P(\theta,\phi)\sin\theta d\theta d\phi = 1 \ . \tag{2}$$

This is equivalent to setting $A_{00} = 1$ in Eq. (1). Eq. (1) is valid for any molecular symmetry, providing that the alignment is created in one dimension only.[20, 21] The number of terms that appear in Eq. (1) limit the anisotropy that is observable in a given measurement. When cylindrical symmetry is maintained, only terms with $Q = 0$ contribute to Eq. (1). In the limit of perfect alignment (all molecular axes lying parallel to the laboratory *Z* axis, with no preference for "up" or "down"), an infinite number of even-*K* values would be needed in the expansion. An isotropic distribution would have $K = 0$, $Q = 0$ only, and a distribution that is oriented as well as aligned (molecular axes lying parallel to the laboratory *Z* axis, with a preference for "up" or "down") requires the presence of non-zero A_{KQ} terms with odd values of *K*.

In general the values of the contributing alignment moments can be determined from a known distribution of molecular axes through the relationship:

$$A_{KQ} = \int_0^{2\pi}\int_0^{\pi} P(\theta,\phi)\frac{Y_{KQ}(\theta,\phi)}{Y_{00}(\theta,\phi)}\sin\theta d\theta d\phi \tag{3}$$

However, the full distribution of molecular axes is generally unknown in a given experiment, and one-dimensional alignment is typically characterized by the single parameter $\langle\cos^2\theta\rangle$,[7, 22] where

$$\left\langle \cos^2\theta \right\rangle = \int_0^{2\pi}\int_0^{\pi} \cos^2\theta P(\theta,\phi)\sin\theta d\theta d\phi \ , \tag{4}$$

or sometimes by the angular width of $P(\theta,\phi)$.[6] Using these measures a perfectly aligned distribution would have $\langle\cos^2\theta\rangle = 1$ (or an infinitesimally small angular width) and an isotropic distribution would have $\langle\cos^2\theta\rangle = 1/3$ (or an angular width of π). Similarly, an oriented distribution can be characterized experimentally by $\langle\cos\theta\rangle$ where

$$\left\langle \cos\theta \right\rangle = \int_0^{2\pi}\int_0^{\pi} \cos\theta P(\theta,\phi)\sin\theta d\theta d\phi \ . \tag{5}$$

Here, an un-oriented distribution would have $\langle\cos\theta\rangle = 0$, and a completely oriented distribution would have $\langle\cos\theta\rangle = 1$ ("up") or -1 ("down").

Although $\langle\cos^2\theta\rangle$ and $\langle\cos\theta\rangle$ give useful experimental measures of alignment and orientation, it is important to understand what values of these parameters are needed if a measurement in the laboratory is to approach the molecular frame. A case in point is the measurement of a photoelectron angular distribution (PAD) resulting from ionization in the weak-field limit. Such a measurement has the potential to image the valence-electron dynamics that occur during a chemical reaction, but only if the molecular frame is approached.[23] The photoelectron wavefunction can be described by an expansion in partial waves defined by the orbital angular momentum, l, with the expansion terminating at l_{max}. In general the photoelectron angular distribution, $I(\theta,\phi)$, can be expressed:

$$I(\theta,\phi) = \sum_{LM} \beta_{LM} Y_{LM}(\theta,\phi) \, . \tag{6}$$

In the molecular frame limit, in which photoelectrons are detected relative to the direction of the principal molecular axis, the PAD will contain terms with $0 \le L \le L_{max}$ and $-L \le M \le L$, up to $L_{max} = 2l_{max}$.[24] In order to assess whether ionization of an aligned distribution of molecules can capture this anisotropy, the alignment needs to be represented in terms of the moments shown in Eq. (1).[20, 21, 25] Direct sensitivity to l_{max} then requires the presence of alignment moments with $K \ge 2l_{max} - 2$. Thus, for

example, if the photoelectron wavefunction contains contributions from *g*-waves (l = 4), these will only be apparent in the laboratory frame PAD if alignment moments with $K \geq 6$ have significant magnitude in the distribution of molecular axes. More generally, high-K alignment moments are needed in order to gain sensitivity to a highly anisotropic experimental observable.

Assuming cylindrical symmetry (Q = 0), and no orientation, it has been shown that when (non-state-selected) molecules interact with a strong electric field the molecular axis distribution in Eq. (1) can often be well-represented using a Gaussian form:[2]

$$P(\theta,\phi) = n_\sigma \exp\left(\frac{-\sin^2\theta}{2\sigma^2}\right), \tag{7}$$

where n_σ is a normalization constant,

$$n_\sigma = \frac{1}{\int_0^\pi \exp\left(\frac{-\sin^2\theta}{2\sigma^2}\right)\sin\theta d\theta} \tag{8}$$

and $0 < \sigma^2 \leq 1$. This form is particularly convenient because the parameter σ^2 relates to the angular width, and for small values of σ^2, is very approximately related to $\langle\cos^2\theta\rangle$ by[2]

$$\lim_{\sigma^2\to 0} \sigma^2 = 1 - \left\langle \cos^2\theta \right\rangle . \tag{9}$$

Although Eq. (9) gives a rule of thumb, the relationship breaks down rapidly as σ^2 increases. Fig. 1a shows the actual relationship between $\langle\cos^2\theta\rangle$ and σ^2, as established using Eq. (4). This figure enables the estimation of σ^2 from an experimentally determined value of $\langle\cos^2\theta\rangle$. It can be seen that the value of $\langle\cos^2\theta\rangle$ has fallen to less than 0.45 by the time that σ^2 has reached 0.5; this represents a negligible degree of alignment.

In some strong-field alignment experiments σ^2 is measured directly; alternatively σ^2 can be determined from an experimentally determined value of $\langle\cos^2\theta\rangle$, using the relationship shown in Fig. 1a. Once σ^2 is known, the alignment moments needed to characterize the molecular axis distribution can be calculated using Eq. (3). The results of this procedure are illustrated in Fig. 1b. Here, $A_{KQ=0}$ coefficients are plotted as a function of σ^2 for values of K up to 16. These plots provide a means of estimating the number of alignment moments that contribute to a distribution described by Eq. (7), as well as the relative values of those alignment moments. It is immediately apparent from these plots that the A_{K0} coefficients decrease rapidly with increasing σ^2, and that higher moments become increasingly significant for small values of σ^2. This is further illustrated in Fig. 2 which shows the values

of σ^2 at which A_{K0} terms with a specified value of K begin to make a significant (> 5% of the value of A_{20}) contribution to the distribution of molecular axes defined by Eq. (7). For example, it can be seen that when $\sigma^2 < 0.1$ ($\langle\cos^2\theta\rangle > 0.76$) the number of moments required to represent the distribution starts to increase rapidly, with $A_{16,0}$ greater than 5% of $A_{2,0}$ for $\sigma^2 < 0.03$ ($\langle\cos^2\theta\rangle > 0.94$). The larger the number of contributing moments the greater the sensitivity to highly anisotropic properties (see below). In experiments in which a single laser pulse is used to create alignment it has been shown that it is not possible to generate values of $\langle\cos^2\theta\rangle$ greater than ~0.76, [9, 26] and that more complicated pulse sequences are required to create higher alignment. A distribution characterized by $\langle\cos^2\theta\rangle \approx 0.76$ gives limited sensitivity to anisotropic properties, as shown below.

Photoelectron angular distributions (PADs) have become a popular probe of non-adiabatic intramolecular dynamics, with their anisotropy uniquely sensitive to purely electronic effects.[23] As discussed above, this sensitivity is maximised if the PADs approach the molecular frame. Calculations of PADs from aligned distributions of molecules therefore provide an excellent illustration of the significance of the plots shown in Figs. 1 and 2. However, in order to be of relevance to experimentalists it is helpful to calculate the PADs that would be expected following ionization of a distribution characterized by $\langle\cos^2\theta\rangle$, rather than choosing an arbitrary set of A_{KQ} values. The alignment parameters needed to describe a Gaussian distribution characterized by a given value of σ^2 provide the means of doing this. A model weak-field molecular frame PAD for an arbitrary symmetric top molecule has been calculated using the formalism of Underwood and Reid,[20] by taking two arbitrary sets of radial dipole matrix elements and phases for partial waves up to $l_{max} = 4$ in order to generate anisotropies that would be averaged out in laboratory frame measurements of molecules that are unaligned, or aligned through resonant excitation with one or two photons. The results of this are shown in Figs. 3 and 4 for the two sets of matrix elements. In both figures panel (a) shows the molecular frame PAD;[§] this has the maximum possible degree of anisotropy, reflecting directly the photoelectron wavefunction. Laboratory frame PADs are then calculated by projecting the molecular frame PAD by convoluting it with distributions of molecular axes described by Eq. (7).

In Fig. 3a it can be seen that the molecular frame PAD has four lobes and so to approach the molecular frame results those same four lobes need to appear in the laboratory frame PAD. The distributions used for the calculations shown in Figs. 3b to 3d are described by $\sigma^2 = 0.06$, 0.1, 0.12, respectively, corresponding to $\langle\cos^2\theta\rangle \approx 0.87$, 0.76 and 0.72. Comparison of the different panels in Fig. 3 allows an assessment of the alignment that needs to be created in order to capture the features of the molecular frame PAD. It can be seen that if the alignment is characterized by $\sigma^2 = 0.1$ ($\langle\cos^2\theta\rangle \approx 0.76$), the

laboratory frame PAD does not contain the necessary four lobes, and in this case σ^2 needs to be at most ~0.06 ($\langle\cos^2\theta\rangle$ > ~0.87) in order for the laboratory frame PAD to resemble the molecular frame PAD. This means that, according to Fig. 2, alignment moments up to K = 10 need to be present in order to reproduce the molecular frame anisotropy in this case. In Fig. 4a radial dipole matrix elements have been chosen to generate a molecular frame PAD with eight lobes. Here, the distributions used for the calculations shown in Figs. 4b to 4d are described by σ^2 = 0.03, 0.06, 0.1, respectively, corresponding to $\langle\cos^2\theta\rangle \approx 0.94, 0.87$ and 0.76, and it can be seen that even an alignment characterized by σ^2 = 0.06 ($\langle\cos^2\theta\rangle \approx 0.87$) is not sufficient to capture the anisotropy of the molecular frame PAD. In this case σ^2 needs to be ~0.03 ($\langle\cos^2\theta\rangle$ > ~0.94) which means that, according to Fig. 2, alignment moments up to K = 16 need to be present. A key result of this work is that the higher the anisotropy present in the molecular frame PAD the better the alignment needs to be in order for a laboratory frame measurement to detect that anisotropy. A deconvolution procedure, designed to extract the molecular frame PAD, can only be applied if the alignment is sufficient for all molecular frame lobes to appear.

A further advantage of characterizing the distribution of molecular axes by Eq. (7) is that this form lends itself to a straightforward extension that allows the representation of an oriented distribution. This can be achieved by writing:

$$P(\theta,\phi) = n_\sigma(1 - a\cos\theta)\exp\left(\frac{-\sin^2\theta}{2\sigma^2}\right), \tag{10}$$

where $-1 \le a \le 1$. Eq. (10) provides a fair representation of some examples of measured and computed oriented distributions of non-state-selected molecules. [1, 9, 11] Using Eq. (10), the alignment remains characterized by σ^2, and the degree of orientation can be characterized by a combination of the parameters a and σ^2, which are related to $\langle\cos\theta\rangle$ by

$$\langle\cos\theta\rangle = -a\langle\cos^2\theta\rangle. \tag{11}$$

The behaviour of $\langle\cos\theta\rangle$ versus a for three different values of σ^2 is shown in Fig. 5a. The value of $\langle\cos\theta\rangle$ is maximized for $\sigma^2 \to 0$ and for $a = \pm 1$. A given value of σ^2 results in the same values of the even-K A_{KQ} coefficients as those shown in Fig. 1b, but a non-zero value of the parameter a means that non-zero $A_{KQ=0}$ coefficients with odd-K also appear. An example of the behaviour of the odd-K $A_{KQ=0}$ coefficients as a function of a is shown in Fig. 5b, for σ^2 = 0.1. The linear relationship is maintained for all values of σ^2, with $A_{KQ=0}$ coefficients with high values of odd-K becoming increasingly important as the value of σ^2 decreases.

The treatment above has assumed cylindrical symmetry throughout, but in some cases the extension to non-cylindrically symmetric experimental geometries is straightforward. A typical scenario might involve a probe laser pulse whose polarization vector lies at some angle β to the alignment axis. Assuming cylindrical symmetry ($Q = 0$) in the original frame, the A_{KQ} parameters in the new frame can be calculated through

$$A_{KQ} = d^K_{0Q}(\beta) A_{K0}, \tag{12}$$

where the $d^K_{0Q}(\beta)$ is a reduced Wigner rotation matrix element that can be calculated using recursion relations.[27] Thus, an experimental determination of $\langle\cos^2\theta\rangle$ would enable the determination of the A_{K0} coefficients relevant to the alignment frame using the procedure outlined above, and these A_{K0} coefficients could be rotated into the probe frame using Eq. (12). The laboratory frame PADs resulting when the probe is an ionizing pulse would also be non-cylindrically symmetric as a consequence of the contribution of β_{LM} terms with $M = Q$ to the expansion in Eq. (6). These PADs could be calculated using the alignment moments determined by Eqs. (3) and (12) to project a given molecular frame PAD into the laboratory frame.

Sophisticated experiments are now able to align asymmetric molecules in three dimensions;[28] in this case cylindrical symmetry is broken in the alignment frame and the spherical harmonics that appear in Eq. (1) are replaced by Wigner rotation matrix elements,[21]

$$D^K_{QQ'}(\alpha,\beta,\gamma) = \exp(-i\alpha Q) d^K_{QQ'}(\beta) \exp(-i\gamma Q'), \tag{13}$$

where (α,β,γ) are the Euler angles necessary to express the orientation of the molecular frame axis system (x,y,z) relative to the laboratory frame axis system (X,Y,Z). Such a situation requires an extension of the treatment given here and will be considered elsewhere.

Conclusion

It has been shown that, when an aligned distribution of molecular axes takes a Gaussian form, the relative magnitudes of the contributing moments of the distribution can be estimated through knowledge of either the angular width (σ^2) or $\langle\cos^2\theta\rangle$. The determination of the alignment moments, which can be achieved through Eq. (3), enables the calculation of the laboratory frame projection of anisotropic molecular properties, such as molecular frame photoelectron angular distributions. These calculations show that $\langle\cos^2\theta\rangle$ needs to approach 0.9 in order to avoid significant blurring to be

caused by averaging. The treatment can be extended quite straightforwardly to oriented distributions, and to non-cylindrically symmetric pump-probe experiments.

Acknowledgement

The research leading to these results has been enabled by funding from the Marie Skłodowska-Curie Actions of the European Union's Horizon 2020 framework under REA grant agreement no. 674960. In particular, I would like to thank the Henrik Stapelfeldt (Aarhus University), a partner in the network, for reading a previous version of this manuscript and making useful comments.

Figure Captions

Fig. 1: (a) $\langle\cos^2\theta\rangle$ as a function of σ^2 for the distribution of molecular axes given by Eq. (7), (b) A_{KQ} alignment moments resulting from Eq. (3) for the distribution given in Eq. (7), as a function of σ^2.

Fig. 2: The values of σ^2 at which A_{K0} terms with a specified value of K begin to make a significant (> 5% of the value of A_{20}) contribution to the distribution of molecular axes defined by Eq. (7).

Fig. 3: Polar plots of photoelectron intensity calculated using the formalism given in Ref. 20 for an arbitrary set of radial dipole matrix elements and phases chosen to generate a distribution with four lobes in the molecular frame. (a) The molecular frame PAD with the polarization vector of the light parallel to the molecular axis, (b)–(d) laboratory frame projection of (a) following the ionization of a Gaussian distribution of molecular axes described by (b) $\sigma^2 = 0.06$ ($\langle\cos^2\theta\rangle \approx 0.87$), (c) $\sigma^2 = 0.1$ ($\langle\cos^2\theta\rangle \approx 0.76$) and (d) $\sigma^2 = 0.12$ ($\langle\cos^2\theta\rangle \approx 0.72$). In (a) Z denotes the molecular axis, in (b)-(d) Z denotes the polarization direction of the linearly polarized ionizing photon, taken to be parallel to the direction of alignment.

Fig. 4: As for Fig. 3 but with radial dipole matrix elements and phases chosen to generate a distribution with eight lobes in the molecular frame. (a) The molecular frame PAD with the polarization vector of the light parallel to the molecular axis, (b)–(d) laboratory frame projection of (a) following the ionization of a Gaussian distribution of molecular axes described by (b) $\sigma^2 = 0.03$ ($\langle\cos^2\theta\rangle \approx 0.94$), (c) $\sigma^2 = 0.06$ ($\langle\cos^2\theta\rangle \approx 0.87$), and (d) $\sigma^2 = 0.1$ ($\langle\cos^2\theta\rangle \approx 0.76$).

Fig. 5: (a) $\langle\cos\theta\rangle$ vs the orientation parameter *a* for three values of σ^2 for a distribution of molecular axes described by Eq. (10). (b) Odd-*K* alignment moments determined using Eqs. 3 and 10 as a function of the parameter *a*, with $\sigma^2 = 0.1$. The experimental degree of orientation is given by Eq. (11).

Notes

‡ Integrals can be straightforwardly evaluated using, for example, *Mathematica*.

§ There is no unique molecular frame PAD. The PAD depends on the relative direction of the electric vector of the ionizing light and the molecular axis.

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